

Distribution and turnover of dissolved DMSP and its relationship with bacterial production and dimethylsulfide in the Gulf of Mexico

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Abstract

We measured the distribution of particulate and dissolved pools of the phytoplankton osmolyte dimethylsulfoniopropionate (DMSP) in the euphotic zone at a series of shelf (<40 m total water depth) and oceanic (>500 m depth) stations in the northern Gulf of Mexico. We also measured turnover rates of the dissolved DMSP pools (DMSPd) with tracer additions of ³⁵S-DMSPd and short-term (<1 h) incubations, with the aim of examining the relationship between DMSPd turnover and bacterial production. Particulate DMSP concentrations were relatively low (<25 nM) throughout the study area with about twofold higher mean concentration at the shelf sites (15 nM) compared with the oligotrophic oceanic sites (7 nM). DMSPd concentrations averaged 3.0 nM in shelf waters and 1.3 nM in oceanic waters. Concentrations of dimethylsulfide (DMS), a degradation product of DMSP, also were low throughout the Gulf, averaging 2.0 nM for all depths sampled and 2.5 nM in surface waters. Microbial assemblages metabolized ³⁵S-DMSPd with the sulfur being incorporated into biomass, volatile compounds (DMS and methanethiol), and other dissolved products. DMSPd turnover was relatively slow (mean of 3.8 nM d⁻¹) in oligotrophic oceanic waters and averaged 10-fold higher (39 nM d⁻¹) in mesotrophic shelf waters. DMS concentrations ranged from 0.2 to 5.1 nM in oceanic waters and appeared to be weakly related to DMSP turnover. In contrast, DMS concentrations in shelf waters fell within a narrow range (0.8–2.8 nM) and showed no relationship at all with DMSPd turnover. DMSPd turnover rates were high enough to sustain the measured concentrations and estimated turnover of DMS, even if the conversion efficiency of DMSPd into DMS was only 10%. DMSPd turnover was significantly correlated with bacterial production (as measured by ³H-thymidine incorporation) and we estimate that DMSPd turnover contributed a mean of 3.4% of the carbon and ~100% of the sulfur required for bacterial growth in Gulf of Mexico surface waters. In addition to its role as a precursor of DMS, DMSP deserves attention as an important substrate for bacterioplankton in the euphotic zone.

Dimethylsulfoniopropionate ((CH₃)₂S⁺CH₂CH₂COO⁻; DMSP) is a sulfur-containing compound that is produced by a wide variety of marine phytoplankton and is distributed throughout the euphotic zone of the oceans (Keller et al. 1989; Kettle et al. 1999). DMSP is present in operationally-defined particulate (DMSPp) and dissolved (DMSPd) forms with the DMSPp pool consisting of filterable phytoplankton and organisms that have accumulated DMSP from their diet. Concentrations of DMSPp typically range from 5 to >300 nM depending on factors such as phytoplankton biomass and species composition (Iverson et al. 1989; Malin et al. 1993). The dissolved DMSP pool is generally smaller (1–50 nM) than the particulate pool, but is believed to be more dynamic, with turnover times estimated to be on the order of hours in subtropical waters (Kiene 1996b; Ledyard and Dacey 1996).

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The biogeochemical cycling of DMSP has come under close scrutiny in recent years because it is the major precursor of dimethylsulfide (DMS) in the ocean. DMS is the principal volatile sulfur compound emitted from the ocean surface to the atmosphere, and this oceanic emission contributes approximately half of the global biogenic flux of sulfur to the atmosphere (Andreae 1990). Natural sulfur emissions contribute to the acidic sulfate aerosol burden in the atmosphere, which in turn plays an important role in climatic processes and atmospheric chemistry (Charlson et al. 1987; Andreae and Crutzen 1997). The rate of DMS emission depends directly on the concentration of DMS in surface waters, which is controlled by complex production and removal processes that are closely tied to food web dynamics and physical factors such as air–sea exchange, water column mixing and photochemistry (Kieber et al. 1996; Dacey et al. 1998; Simó and Pedrós-Alió 1999). Although DMSPd has been suggested as the source of most DMS (Turner et al. 1988), considerable uncertainty remains concerning the relationship between DMS production and that of DMSP turnover under in situ conditions.

With the emphasis of most DMSP research focused on its role as a source of atmospheric DMS, less effort has been placed on understanding the importance of this compound in the food web. However, a growing body of evidence suggests that DMSP could be a quantitatively significant compound in the carbon and sulfur cycles within marine pelagic communities. DMSPp often contributes significantly to the total particulate organic sulfur in the euphotic zone (Bates

et al. 1994; Matrai and Vernet 1997). DMSP also represents a significant fraction (1–16%) of the cellular organic carbon in certain phytoplankton cultures (Matrai and Keller 1994) and in field populations (Bates et al. 1994). Once released from phytoplankton, either by direct excretion, grazing, or viral lysis, DMSPd is rapidly degraded (Kiene 1996b; Ledyard and Dacey 1996) and probably utilized as a growth substrate by bacteria (Ledyard and Dacey 1994; Yoch et al. 1997; González et al. 1999). Marine bacteria degrade DMSP either to DMS or to other sulfur compounds including the highly reactive species, methanethiol (MeSH) (Kiene 1996a). Recently another ecologically-important function of DMSP was discovered; it serves as a major source of sulfur for bacterial protein synthesis (Kiene et al. 1999). Because of the sizable pool of DMSP in seawater and because it is a labile carbon and sulfur substrate for marine bacteria, the turnover rate of this compound is of interest from both ecological and biogeochemical perspectives.

To date most studies of DMSP cycling have relied upon experiments in which DMSPd has been added to seawater at concentrations significantly above those present naturally (Kiene 1996b; Ledyard and Dacey 1996). This approach, although useful for providing potential DMSPd turnover rates and information about the sulfur gases produced, suffers from the problems associated with artificially increasing substrate levels above ambient levels, and with the long incubation times (usually many hours) required to observe changes in DMSP/DMS pool sizes by the gas chromatography methods typically employed.

In the present study, we measured the turnover rate constants of DMSPd in epipelagic waters in the Gulf of Mexico with tracer-level additions of ^{35}S -DMSP. The concentrations of DMSPd, DMSPp, and DMS also were measured allowing us to calculate in situ DMSPd turnover rates and to investigate how these rates were related to the concentrations of sulfur compounds. The relationship between DMSPd turnover and bacterial production was examined and we estimated the quantitative contribution of DMSP to the carbon and sulfur demand of bacterioplankton.

Methods and Materials

Study area—All data presented here were collected in the northern Gulf of Mexico aboard the R/V *Pelican* in September 1997. The cruise track and major sampling locations are shown in Fig 1. Detailed information about the station locations and the water mass characteristics are given in Table 1. Sta. 1, 8, 18, and 23 had total water depths of less than 40 m and are referred to as shelf stations. Sta. 2, 5, 10, 12, and 14 had total depths ranging from 540 to 3,184 m, and are referred to as oceanic stations. On the basis of low surface nitrate and chlorophyll concentrations (Table 1) the oceanic sites were characterized as oligotrophic, which is typical of offshore waters in the northeastern Gulf of Mexico. The shelf sites varied in character from relatively oligotrophic to mesotrophic ($\text{NO}_3^- + \text{NO}_2^- < 4 \mu\text{M}$) with only one surface sample in the Mississippi River discharge (Sta. 23) having a very high nitrate concentration ($22 \mu\text{M}$).

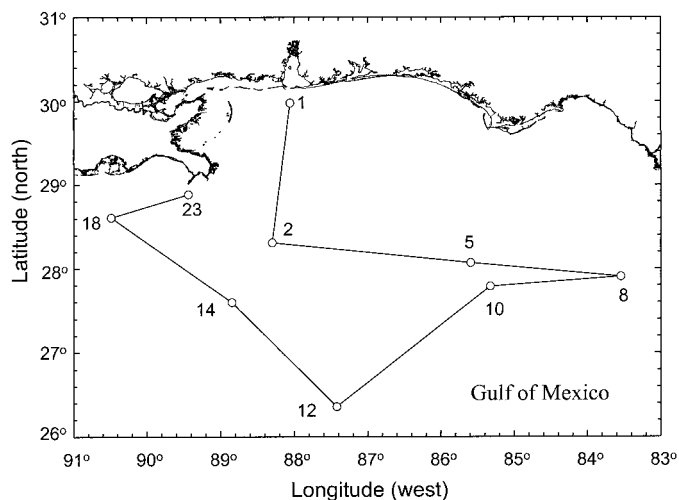


Fig. 1. Map of the northern Gulf of Mexico showing the cruise track of the RV *Pelican* and the location of sampling stations. The cruise took place from 23 September 1997 to 2 October 1997.

Sampling—All water samples were collected in 5-liter Niskin bottles deployed on a rosette equipped with a SeaBird Electronics CTD package. All samples used for DMSP turnover and other rate measurements were collected on casts made in the early morning, 0600–0730 h, a time at which bacterial and phytoplankton populations are minimally affected by exposure to daily ultraviolet radiation (Aas et al. 1996). At each station, four depths within the upper 100 m were sampled for rate determinations (*see below*). Samples for DMSP and DMS concentration measurements were collected at these four depths and occasionally several other depths within the euphotic zone.

DMSP and DMS concentration measurements—Water samples from Niskin bottles were collected in acid-rinsed 250 ml polycarbonate bottles. Processing commenced immediately, but some samples were held at in situ temperature in the dark for up to 3 h before processing could be completed. For DMSPp and DMSPd determinations, 50 ml subsamples (in duplicate) were removed after gently inverting the sample bottle several times. Each 50-ml subsample was filtered through a 47-mm Whatman GF/F filter ($0.7 \mu\text{m}$ nominal retention) by using gravity only. DMSP on the filter (DMSPp) or in the filtrate (DMSPd) was quantified by gas chromatography after its conversion to DMS by alkaline hydrolysis (Kiene 1996b). Dissolved DMS and MeSH concentrations were determined in duplicate on 2 or 4 ml subsamples as described in Kiene (1996b). Sulfur gas analyses were calibrated with a permeation system (Dynacalibrator; VICI Metronics). Detection limits for DMS and DMSP were between 0.2 and 0.5 nM for the water volumes processed. Precision of replicate DMSP or DMS determinations during the cruise was better than 15%. MeSH was below the detection limit ($<0.2 \text{ nM}$) for all samples reported here.

DMSP turnover rates—DMSPd turnover rate constants were determined by adding ^{35}S -DMSP at nonperturbing concentrations ($<0.1 \text{ nM}$). We used duplicate 20 ml seawater

Table 1. Station locations and water mass characteristics, including DMSP and DMS concentrations for R/V *Pelican* cruise in the northern Gulf of Mexico, September, 1997. ND = not detectable (<0.01 nM).

Station no.	Date	LAT	LON	Total depth (m)	Sample depth (m)	Temperature (°C)	Salinity (psu)	Chl <i>a</i> ($\mu\text{g L}^{-1}$)	NO ₃ + Nitrite (μM)	[DMSPd] (nM)	[DMSPp] (nM)	DMS (nM)	DMSPp/Chl <i>a</i> (nmol μg^{-1})
Shelf sites													
1	22 Sep 97	29 58.72	88 3.49	32	1	29.6	32.66	0.21	0.12	4.5	11.0	2.5	54
8	25 Sep 97	27 54.14	83 32.63	35	10	29.22	35.05	0.14	ND	3.6	10.9	2.8	76
					25	29.2	35.05		ND	3.0	10.5	2.5	
					33	29.95	36.29		ND	2.5	17.6	1.3	
18	29 Sep 97	28 36.54	90 29.19	27	1	24.98	36.17		0.92	3.4	21.3	2.9	
					6	27.69	31.39	0.35	0.02	1.0	9.2	1.8	26
					14	28.53	33.11	0.22	ND	1.7	11.6	1.3	53
					24	28.96	35.51	0.34	ND	3.1	10.2	0.8	30
23	30 Sep 97	28 53.12	89 26.20	16	1	25.2	36.08	0.15	1.76	10.0	15.9	2.1	104
					3	28.21	27.54	3.2	22.1	1.0	13.8	2.3	4
					5	28.22	28.07	1.0	1.21	1.7	23.9	2.4	24
					10.5	28.26	29.18	4.7	1.17	1.7	20.1	2.1	4
					Means	28.07	32.73	3.2	3.79	1.9	15.8	1.5	5
						28.16		1.4		3.0	14.7	2.0	38.0
Oceanic sites													
2	23 Sep 97	28 22.82	88 17.97	2280	1	29.03	35.73	0.10	0.02	2.0	8.5	3.0	85
					10	29.02	35.73		0.01	1.8	6.6	3.0	
					20	28.74	35.95		ND	0.6	7.6	2.2	
5	24 Sep 97	28 04.04	85 35.67	540	35	26.95	36.29		0.05	1.8	6.0	1.4	
					1	29.98	35.08	0.089	ND	1.9	6.4	4.4	72
					10	28.97	35.09		ND	1.7	7.0	5.1	
					20	29.00	35.1		ND	1.3	8.2	4.6	
10	26 Sep 97	27 04.72	85 19.56	3184	35	26.85	36.28		ND	2.5	6.2	2.5	
					1	29.01	35.08	0.088	0.06	0.9	6.2	2.8	70
					10	29.00	35.08	0.088	ND	0.3	6.4	1.3	73
					24	28.79	35.75	0.100	0.01	0.2	6.7	0.3	67
12	27 Sep 97	26 21.57	87 25.28	2964	73	21.79	36.45	0.80	0.71	0.4	6.0	0.2	7
					1	28.96	36.16	0.082	0.05	1.6	4.4	0.8	54
					10	28.89	36.15	0.088	ND	0.8	5.8	0.9	66
					30	28.87	36.15	0.092	ND	1.0	5.4	0.8	59
14	28 Sep 97	27 35.76	88 50.99	1833	100	26.94	36.3	0.51	0.34	1.1	4.1	0.6	8
					1	28.99	35.73	0.11	0.13	1.7	7.3	2.4	67
					10	28.99	35.81	0.11	0.01	1.0	7.6	2.3	68
					67	23.59	36.31	0.36	0.04	2.6	9.1	0.4	25
					Means	27.97		0.20		1.3	6.6	2.1	56

samples from each of four depths in the upper 75 m of the water column. Approximately $1\text{--}1.5 \times 10^4$ dpm of ^{35}S -DMSP (3 Ci mmol^{-1} ; synthesized according to Kiene et al. [1998]) was added to each 20 ml sample. Samples were incubated in 50 ml polypropylene centrifuge tubes in the dark at the surface water temperature (flow through incubator; 28–29°C). Deeper water samples that had temperatures at or below 26°C were incubated at 25–26°C. The fraction of added ^{35}S -DMSPd converted into particulates and volatiles (*see below*) during incubations of 0.2–1 h was used to estimate the turnover rate constants of the DMSPd pool. Sample uptake and volatile production were corrected for time zero or killed controls, the latter consisting of water samples treated with sodium dodecylsulfate (SDS; 0.2% final concentration) (Ledyard and Dacey 1994). The rate of DMSPd turnover was calculated from the measured rate constants (k) multiplied by the concentration of DMSPd measured in water from the same depth.

$$\frac{d\text{DMSPd}}{dt} = k[\text{DMSPd}]$$

The calculation assumes steady state for the concentration of DMSPd, which is reasonable given the short incubation times used (<1 h).

During short incubations (<1 h), as used here, up to 30% of the transformation products from ^{35}S -DMSP could be in a dissolved non-volatile pool (Kiene and Linn, submitted). The dissolved nonvolatile ^{35}S products were not accounted for in the measurements made during the cruise in 1997, therefore turnover rate constants were underestimated and the true rates of DMSP turnover were up to 43% higher than we report here. Failure to account for the ^{35}S -nonvolatile products undoubtedly contributed to variability in measured rates, but the underestimation of rates makes conclusions about the quantitative significance of DMSP turnover conservative (*see Discussion*).

Time courses of ^{35}S -DMSP uptake—Several incubations were carried out to evaluate the time dependence of product formation from ^{35}S -DMSPd. Samples were treated with tracer levels of ^{35}S -DMSP and incubations were carried out as described above, except that larger volumes of samples were incubated so that subsamples could be withdrawn at selected time points over 1 or 25 h depending on the experiment. The amount of ^{35}S in filterable particulates ($>0.2 \mu\text{m}$) and volatiles was measured at each time point. In one incubation subsamples were collected on filters for extraction of untransformed ^{35}S -DMSP that was retained in bacterial cells. The procedures for extracting and quantifying the cellular ^{35}S -DMSP are described in Kiene and Linn (1999).

Determination of uptake and volatiles production from ^{35}S -DMSP—In both time course and turnover rate incubations, uptake of ^{35}S (from ^{35}S -DMSP) into particulates was determined by filtering 10 ml from each replicate incubation tube through 0.2- μm Supor (polyethersulfone; Gelman) membrane filters with a Hofer filtration manifold and low (<10 cm Hg) vacuum. Filters were rinsed with 3×1 ml of 0.2- μm filtered seawater before they were removed and placed in scintillation vials with 5 ml of Ecolume scintilla-

tion cocktail (ICN Biomedicals). Radioactivity was determined at sea with a Packard scintillation counter. Final, more reliable, counts for the samples were obtained on shore after the cruise, and, if necessary, were corrected for decay of ^{35}S ($\tau_{1/2} = 87.3$ d). Volatile ^{35}S produced from ^{35}S -DMSP was collected by pipetting the remaining 10 ml of each sample into a 120 ml serum bottle which contained 0.2 ml of 10% SDS to stop further uptake of DMSP (Ledyard and Dacey 1994). After transfer of the sample, the bottles were quickly sealed with rubber stoppers fitted with suspended plastic cups (Kontes). The cups contained a pleated 25 mm glass fiber filter (Gelman AE) soaked with 0.3 ml of 3% H_2O_2 . Bottles were placed on a gyratory shaker for >6 h, after which time ^{35}S volatiles became trapped in the H_2O_2 -soaked filters. After the trapping period, the cups (with the filters) were clipped from the stoppers and placed directly into 10 ml of Ecolume for determination of trapped ^{35}S activity. Tests showed that this method trapped >80% of MeSH and >90% of DMS, the two most likely volatile sulfur compounds to be produced from DMSP. Because the method does not distinguish between these gases we refer to this fraction simply as ^{35}S -volatiles. Extensive testing showed that total recovery of added ^{35}S in the liquid phase of water samples incubated 1–2 h was >98%; for incubations lasting ~30 h it was >95%. This indicated that losses of ^{35}S due to volatilization or adsorption to the container were minimal.

Thymidine incorporation and bacterial production—The tritiated thymidine (TdR) method was used for estimating bacterial growth and carbon production (Fuhrman and Azam 1982). Briefly, 45 ml samples were incubated in acid cleaned 50 ml Corning centrifuge tubes (polypropylene). Four replicates per depth were used with one being killed at time zero by addition of 5 ml of 50% trichloroacetic acid (TCA). Each tube received ca. 1.7 μCi of methyl- ^3H -thymidine (4 Ci mmol^{-1}) to give added concentrations of 10 nM ^3H -TdR. After an incubation period (1–3 h depending on the station), incorporation of the 3H label into cellular macromolecules (insoluble in cold 5% TCA) was quantified by filtration of samples onto 0.2- μm Supor filters. Filters were counted in 5 ml of Ecolume with a liquid scintillation counter. Results are reported as pM TdR incorporated per hour. These data were used to estimate bacterial cell production assuming a conversion factor of 2×10^{18} cells per mole of TdR incorporated. We verified that this conversion factor was appropriate for coastal Alabama waters, but we did not do this at each of the offshore sites. Bacterial carbon production was estimated with a per-cell carbon content of 2×10^{-14} gC per cell (Lee and Fuhrman 1987). Finally, bacterial carbon demand was estimated by use of the measured production values and an assumed bacterial growth efficiency (BGE) of 0.25 (cell carbon produced divided by carbon utilized). We elected to use this value because it is close to that measured previously in shelf and slope waters of the Gulf of Mexico (Chin-Leo and Benner 1992; Biddanda et al. 1994).

Community respiration—Respiration of oxygen in the dark was measured to provide an estimate of plankton community metabolism and an overall constraint on the bacterial carbon utilization (Jahnke and Craven 1995). Rate estimates

were obtained only from surface waters at each station. Multiple 60ml BOD bottles (15–18) were filled from a single Niskin bottle and incubated in the dark at the in situ temperature. Five or six of the replicate bottles were fixed with Winkler reagents at 0, 12, and 24 h. Dissolved oxygen concentrations were measured on shipboard by the Winkler method (Strickland and Parsons 1968) with a Mettler DL-21 autotitrator. Precision for replicate samples was typically better than 0.5%. The change in O_2 concentration vs. time was linear for all stations and the linear regression slopes were statistically significant ($P < 0.05$) in all cases.

Other measurements—Chlorophyll *a* in particulate material captured on Whatman GF/F filters was determined by fluorometry as described in Strickland and Parsons (1968). Nitrate was determined by autoanalysis on an Alpkem model RFA/2.

Results

Oceanographic setting—Sea surface temperatures were similar at all stations, ranging from 28–29°C. Oceanic sites were characterized by extremely low, often undetectable nitrate concentrations within the euphotic zone (Table 1). Chl *a* concentrations in surface waters from oceanic stations were very low (0.088–0.11 $\mu\text{g Chl } a \text{ L}^{-1}$) and Chl *a* maxima (up to 0.8 $\mu\text{g Chl } a \text{ L}^{-1}$) were typically at depths from 40–75 m. Colonies of the filamentous nitrogen fixing cyanobacterium *Trichodesmium* sp. were observed in surface waters at all oceanic stations but we did not quantify these organisms. Shelf sites had higher and more variable nutrient and Chl *a* levels (0.14–4.7 $\mu\text{g Chl } a \text{ L}^{-1}$), especially at stations influenced by the Mississippi River plume. Shelf stations had complex vertical structure in the water column, controlled by gradients in both temperature and salinity. We therefore used the density (σ_t) to define the water column structure (see Figs. 2, 3). Oceanic sites generally had well mixed water columns to depths of 10–45 m. Below the mixed layer, a pronounced Chl *a* maximum was observed in all oceanic stations (Table 1). All samples for rate determinations at oceanic stations came from depths at or above the chlorophyll maximum (see below).

DMSP, and DMS concentrations—For all stations the DMSPp concentrations ranged from 4.0–23.9 nM with a mean value of 15.1 nM at shelf sites and 6.6 nM at oceanic sites. The DMSPd concentrations were lower than the particulate pool and ranged from a low of 0.2 nM at the most oligotrophic station (Sta. 10), to a high of 10.0 nM at the near bottom depth of 24 m at station 18 on the Louisiana shelf (Table 1; see also Figs. 2, 3). The average DMSPd concentration at shelf sites was 3.0 nM, whereas it was 1.3 nM at oceanic sites. DMS concentrations ranged from 0.2 nM at Sta. 10 (73 m depth), to a high of 5.1 nM at Sta. 5 (10 m depth). The mean DMS concentrations of shelf (2.0 ± 0.06 nM) and oceanic (2.1 ± 1.7 nM) sites were not significantly different.

DMSP:Chl *a*—The DMSP:Chl *a* ratio (nmol: μg) in particulate material was relatively high throughout the Gulf of

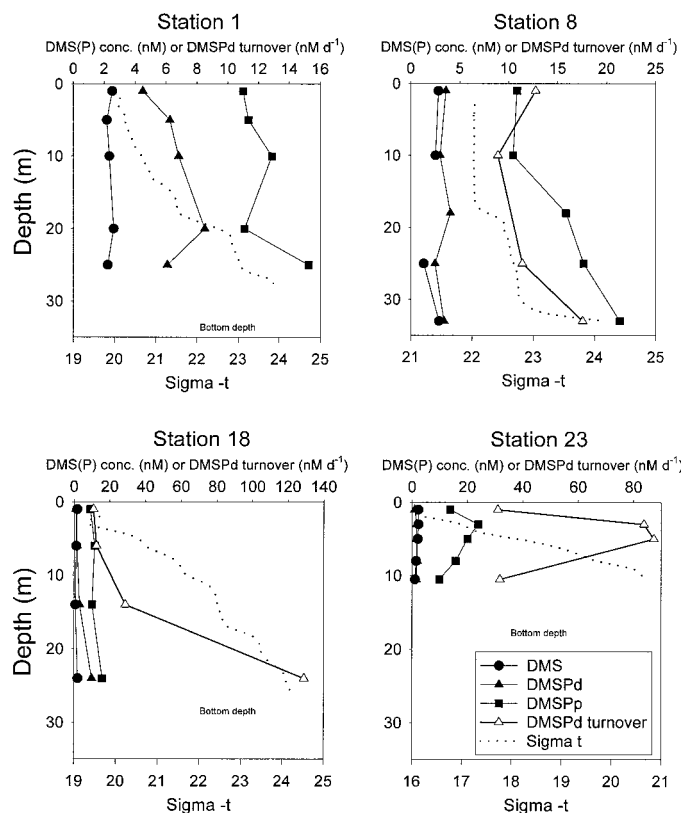


Fig. 2. Depth profiles of DMSPp, DMSPd, and DMS concentrations as well as turnover rates of DMSPd for sampling stations located on the continental shelf (water depths <40 m) in the northern Gulf of Mexico. Station locations are shown in Fig. 1.

Mexico with mean values of 38 for shelf sites and 56 for oceanic sites (Table 1). Relatively low DMSP:Chl *a* ratios (4–25) were found in samples from below the mixed layer of oceanic stations and at Sta. 23, near the mouth of the Mississippi River. These low ratios can be attributed mostly due to the higher Chl *a* concentrations at the shelf sites and at the subsurface chlorophyll maximum of the oceanic stations.

Time courses of ^{35}S -DMSP uptake and degradation—A time course conducted with surface water from Station 1 showed that uptake of ^{35}S -DMSP into filterable particulates and conversion into ^{35}S volatiles was approximately linear for at least 60 min (Fig. 4). The rate of product accumulation (^{35}S -particulates + volatiles) in this experiment was equivalent to 17% of the added tracer per hour. In contrast, the uptake of labeled DMSP in a water sample treated first with 0.1% SDS was negligible (Fig. 4). During the early part of incubations volatile and particulate ^{35}S comprised roughly similar percentages of the quantified end products (Fig. 4). For all of our DMSP turnover experiments (0.2–1 h incubations) the average ratio of volatile to particulate ^{35}S end-products was 0.68 with no significant difference between shelf and oceanic stations.

A longer incubation (25 h) was carried out at Sta. 14 in order to determine the fate of DMSP sulfur after all the added ^{35}S -DMSPd had been utilized. Accumulation of ^{35}S in

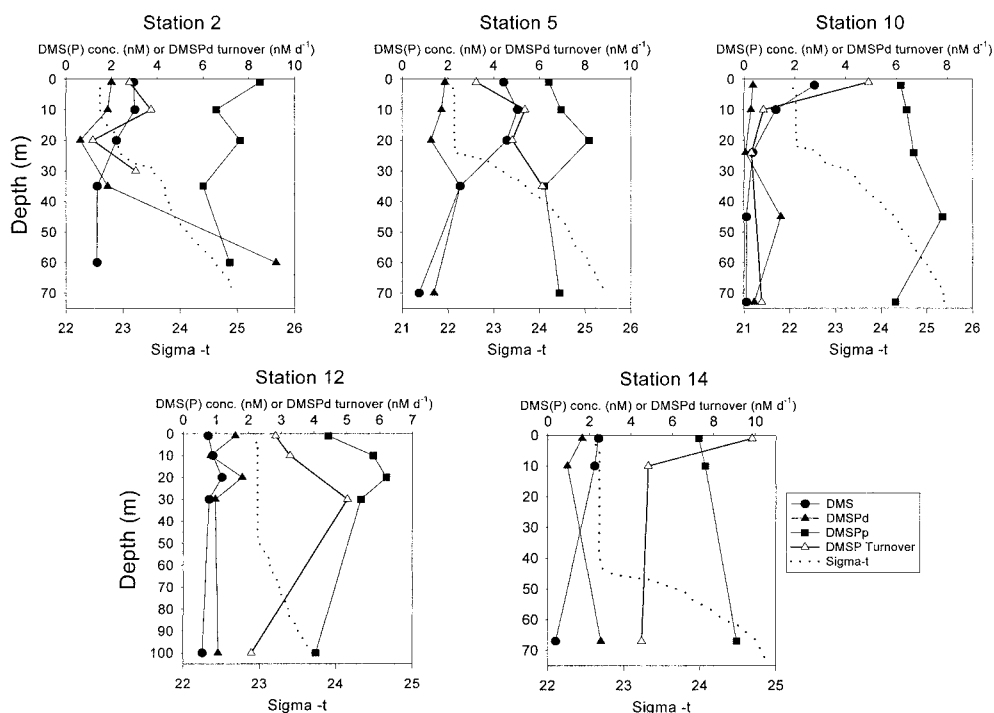


Fig. 3. Depth profiles of DMSPp, DMSPd, and DMS concentrations as well as turnover rates of DMSPd for oceanic stations (water depths >500 m) in the northern Gulf of Mexico. Station locations are shown in Fig. 1.

filterable particles was rapid for the first 3 h, followed by a period of slower increase from 3–25 h (Fig. 5). Particle-associated ^{35}S represented 24% of the added label at the end of the incubation. Early in the incubation a significant fraction (>50%) of the total particulate ^{35}S was untransformed ^{35}S -DMSP, presumably in bacterial cells. This intracellular

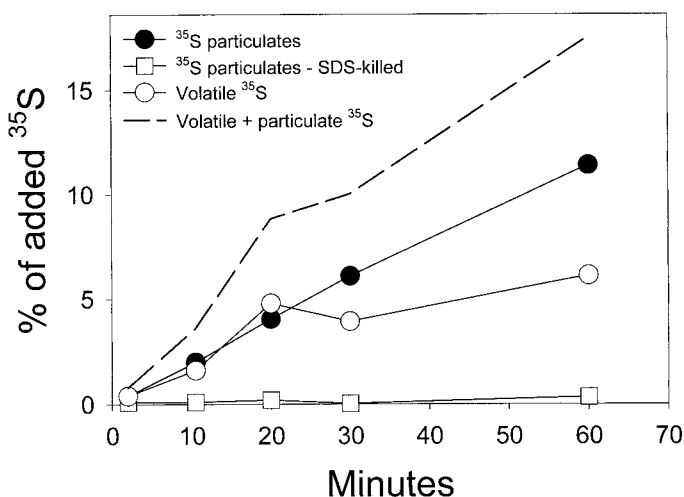


Fig. 4. Short-term time course of ^{35}S -DMSP uptake and volatile product formation obtained with surface water from Sta. 1. Data values represent the amount of ^{35}S (dpm) recovered in each fraction from 10 ml subsamples at each time point. The dashed line represents the sum of filterable plus volatile ^{35}S . Incubation was in the dark at 29°C. Also shown is the total uptake by a seawater sample treated with 0.1% SDS just prior to ^{35}S -DMSP addition.

accumulation of the added tracer was transient and began to decline after 2 h. By 12 h the untransformed ^{35}S -DMSP in cells was only 10% of the total particulate ^{35}S (equivalent to 2.2% of the total added label). Volatile ^{35}S accumulated transiently, with a peak at 4–5 h equivalent to 14% of the added ^{35}S by end of the incubation (Fig. 5). The time course of quantified end-products (particles + volatiles; dotted line in Fig. 5) suggested that most of the added ^{35}S -DMSP was degraded after 12 h. A test at the end of the incubation (25 h) involving alkaline hydrolysis of any remaining ^{35}S -DMSP and trapping of the resulting ^{35}S -DMS confirmed that >95% of the added ^{35}S -DMSPd had been degraded by the seawater microorganisms. However, the maximum recovery of end products (volatile + particulate ^{35}S) after 25h was only 30% of the added label, therefore other dissolved products must have been formed. Subsequent to the cruise, we discovered that dissolved, nonvolatile ^{35}S compounds, including $^{35}\text{SO}_4^{2-}$ and complexes of ^{35}S -MeSH, were major transformation products of ^{35}S -DMSP that were not quantified during the September 1997 cruise (see Discussion). We reiterate that in short term incubations, such as those used for rate determinations, dissolved, nonvolatile products were probably less than 30% of the total transformation products.

Rates of DMSPd turnover and vertical profiles of DMSPp, DMSPd, DMS—Concentrations of methylated sulfur compounds are shown together with the DMSPd turnover rates in Fig. 2 for shelf stations and Fig. 3 for oceanic stations. DMSPd turnover appeared to be highest at mid-depths within the euphotic zone, although at station 10, the highest rate

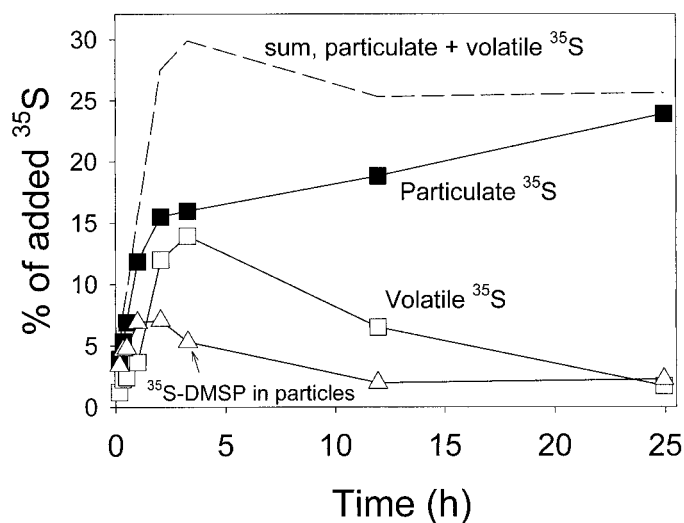


Fig. 5. Time course of ^{35}S -DMSP uptake and volatile product formation obtained with surface water from Sta. 14. Data values represent the amount of ^{35}S (dpm) recovered in each fraction from 10 ml subsamples at each time point. Also shown is the amount of ^{35}S activity in particulate material that was untransformed substrate (^{35}S -DMSP). The dashed line represents the sum of filterable plus volatile ^{35}S . Incubation was in the dark at 28–29°C.

was in the sample from 1 m. The pattern of DMSPd turnover seemed to follow that of DMSPp at several stations (8, 23, and 12), but was less obvious at other stations. However, the overall relationship between these variables was statistically significant ($r^2 = 0.500$; $n = 31$; $P < 0.001$). There was no obvious relationship between DMSPd turnover and DMSPd concentration ($r^2 = 0.03$; $P = 0.32$), nor with the vertical density distribution. DMS maxima, if present, were typically observed in the upper 20 m and DMS appeared to be weakly related to DMSPd turnover rate in offshore stations, but not at inshore stations (see below).

DMSPd turnover vs. DMS concentration—Considering data separately from shelf and oceanic sites, there appeared to be two distinct patterns between DMSP turnover and DMS concentrations (Fig. 6). At shelf stations, DMSPd turnover was relatively high and varied over a 10-fold range (10–129 nM d⁻¹) (Table 2). Despite the relatively high DMSPd turnover, DMS concentrations were low (mean = 2.0 nM) and varied over a narrow range (0.8–2.9 nM; Fig. 6). There was no relationship between DMSPd turnover and DMS concentration ($r^2 = 0.001$) for the shelf stations. DMSPd turnover at oceanic sites, was lower than on the shelf (2.8–14 nM d⁻¹), and the mean DMS concentration at these stations (2.1 nM) was similar to that in shelf waters. The offshore DMS concentrations varied over a larger range (0.2–5.1 nM) than at inshore sites, primarily due to higher concentrations at Sta. 5. At the oceanic stations there was a weak linear relationship between DMSPd turnover and DMS concentration ($P = 0.08$) but the variation in DMSPd turnover explained only a small fraction of the variation in DMS concentration ($r^2 = 0.167$).

TdR incorporation and dark O₂ respiration—TdR incorporation rates, an estimate of bacterial production, were low in oceanic waters, ranging from 14 to 124 pM TdR h⁻¹ (Table 2). Much higher rates were found in shelf waters (126–2466 pM TdR h⁻¹). Respiration of O₂ was correspondingly low at oceanic stations (0.8–1.0 μM O₂ d⁻¹) and higher in shelf stations (1.6–10.5 μM O₂ d⁻¹) (Table 2). When we used a bacterial growth efficiency of 0.25 and the measured bacterial carbon production rates, the estimated contribution of bacteria to community respiration averaged 105%.

DMSP turnover vs. bacterial production—For all stations and depths, the rate of DMSPd turnover was significantly correlated with the rate of bacterial production ($y = 0.66x + 4.56$; $r^2 = 0.72$; $n = 31$; $P < 0.001$; Fig. 7). There were few points with intermediate rates because we sampled either in oceanic waters or in nearshore shelf waters. One point, with very high DMSPd turnover was excluded from the correlation because this sample came from a near bottom cast at a shallow site and had a relatively high DMSPd concentration compared with all the other stations (see Fig. 7), possibly due to sediment influences. If this anomalous point is included, the overall relationship was still significant ($P < 0.001$).

Discussion

Distribution of DMSP and DMS—DMSP, the biogenic precursor of DMS in seawater, is produced nearly exclusively by photoautotrophic algae, but the factors that control its distribution are not well known. Likewise, the mechanisms by which DMS is produced from DMSP are not well understood. Prior to this investigation, few data were available on the concentrations and distribution of DMSP and DMS in the Gulf of Mexico. Andreae and Raemdonck (1983) reported an average DMS concentration in the Gulf of Mexico of 1.63 nM ($n = 4$). In the present study, which covered only a 10-d period in late summer, we found low concentrations of both DMSP (<25 nM) and DMS (<5.5 nM) throughout the northern Gulf (Table 1). The low concentrations of DMSP and DMS are consistent with the generally low nutrient and Chl *a* levels present during our sampling. The mean DMS concentration that we measured in surface waters (2.5 nM) was fortuitously identical to the world-wide average of 2.5 nM for low and mid-latitude oceanic waters (Kettle et al. 1999), and slightly higher than the value reported earlier by Andreae and Raemdonck (1983). Other studies have shown that above-average concentrations of DMSP and DMS are mainly associated with blooms of DMSP-producing phytoplankton (Malin et al. 1993). The highest DMSP and DMS concentrations so far measured in the Gulf of Mexico were observed previously in coastal waters near Dauphin Island Alabama, where elevated concentrations of DMSPp (~150 nM), DMSPd (~12 nM), and DMS (11 nM) were occasionally observed associated with dinoflagellate blooms (Kiene 1996b). Those concentrations and the ones measured in the present study, are low in comparison to the enormous (>1,000 nM) concentrations of DMSPp sometimes associated with blooms of *Phaeocystis*

Table 2. Bacterial production, oxygen respiration and DMSPd turnover rates in water samples from shelf and oceanic sites in the Northern Gulf of Mexico. Also shown is the calculated bacterial carbon demand and the contribution of DMSP to that demand.

Station	Sample depth (m)	Thymidine uptake (pM d ⁻¹)	Calculated bacterial production* (μM C d ⁻¹)	Calculated bacterial C demand† (μM C d ⁻¹)	O ₂ respiration (μM day ⁻¹)	DMSPd turnover (nM d ⁻¹)	Carbon turnover through DMSP (μM DMSP-C d ⁻¹)	Contribution of DMSP to bacterial carbon demand† (%)
Shelf sites								
8	1	126	0.42	1.68	1.59	12.8	0.064	3.80
	10	167	0.56	2.22		8.9	0.045	2.00
	25	250	0.83	3.33		11.4	0.057	1.71
	33	449	1.50	5.99		17.5	0.088	1.46
18	1	368	1.23	4.90	3.77	10.9	0.055	1.11
	6	223	0.74	2.97		12.6	0.063	2.12
	14	183	0.61	2.43		28.7	0.144	5.90
	24	294	0.98	3.91		129	0.645	16.5
23	1	2470	8.22	32.9	10.5	31.0	0.155	0.47
	3	2340	7.81	31.2		83.8	0.419	1.34
	5	1930	6.45	25.8		87.4	0.437	1.69
	10.5	379	1.26	5.05		31.8	0.159	3.15
	Means	765	2.55	10.2	5.3	38.8	0.194	3.44
Oceanic sites								
2	1	42.0	0.14	0.56	no data	2.78	0.014	2.48
	10	24.7	0.08	0.33		3.73	0.019	5.67
	20	50.7	0.17	0.68		1.18	0.006	0.87
	35	22.7	0.08	0.30		3.05	0.015	5.05
5	1	46.7	0.16	0.62	0.94	3.23	0.016	2.59
	10	58.0	0.19	0.77		5.37	0.027	3.47
	20	62.7	0.21	0.84		4.81	0.024	2.88
	35	60.9	0.20	0.81		6.13	0.031	3.78
10	1	124	0.41	1.65	0.93	4.90	0.025	1.48
	10	75.1	0.25	1.00		0.77	0.004	0.38
	24	52.1	0.17	0.69		0.29	0.001	0.21
	73	13.9	0.05	0.19		0.70	0.003	1.88
12	1	44.5	0.15	0.59	0.80	2.82	0.014	2.37
	10	43.4	0.14	0.58		3.27	0.016	2.83
	30	31.6	0.11	0.42		5.02	0.025	5.95
	100	21.3	0.07	0.28		2.09	0.010	3.69
14	1	87.8	0.29	1.17	1.01	9.85	0.049	4.21
	10	68.1	0.23	0.91		4.84	0.024	2.67
	67	26.1	0.09	0.35		4.53	0.023	6.50
	Means	50.3	0.17	0.67	0.90	3.65	0.018	3.10

* Bacterial production was calculated from the thymidine incorporation rates assuming 2×10^{18} cells were produced per mole of thymidine incorporated, and that each cell contained 2×10^{-14} g of carbon.

† A bacterial growth efficiency (cell carbon production/(cell carbon production + respiration)) of 0.25 was assumed for the calculations of carbon demand.

sp. in the coastal North Sea-Wadden Sea area (van Duyl et al. 1998).

Judging by the low Chl *a* concentrations, no major phytoplankton blooms were encountered during the 1997 cruise. The few stations we sampled close to the discharge of the Mississippi River (Sta. 18 and 23; Table 1) had higher nutrient and Chl *a* levels (up to $4.7 \mu\text{g L}^{-1}$) but also had high turbidity, which probably limited phytoplankton biomass and DMSP accumulation. In addition, coastal phytoplankton assemblages in river plumes are typically dominated by diatoms, which are known to have relatively low DMSP per unit biomass (Keller et al. 1989). Although we did not determine the phytoplankton species composition, the low

DMSP:Chl *a* ratios (4–24) we observed near the mouth of the Mississippi River (Sta. 23), would be consistent with a diatom dominated assemblage. In contrast nearly all the other stations showed DMSP:Chl *a* ratios of >30 (Table 1), which are more typical of oceanic picoplanktonic assemblages (Iverson et al. 1989). In the field, several factors appear to be important in controlling DMSP distribution including the phytoplankton species composition, nutrients, light, and the stage of blooms (Malin et al. 1993; Matrai and Keller 1993). Laboratory work with phytoplankton cultures has shown that variations in DMSP production among phytoplankton can span several orders of magnitude (Keller et al. 1989). Furthermore, variations in DMSP content within

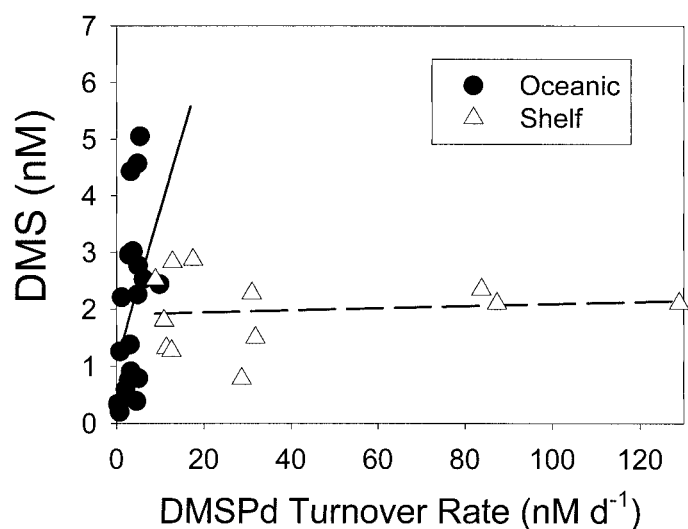


Fig. 6. Plot of DMS concentrations vs. DMSPd turnover rate for oceanic and shelf sites. The lines represent linear least squares regression fits to the data. For the oceanic sites the relationship was $\text{DMS} = 0.270x + 1.06$; $r^2 = 0.167$, $n = P = 0.08$).

a single species also can be significant, being dependent on nutrient status, light, clonal lineage as well as other poorly understood factors (Matrai et al. 1995; Keller and Korjef-Bellows 1996).

The flux of DMS from the oceans to the atmosphere is an important part of the global sulfur cycle (Andreae and Raemdonck 1983; Andreae 1990) and is driven in large measure by the concentrations of DMS in surface waters together with the wind speed. Unfortunately the data set collected here are too limited in space and time to permit a meaningful calculation of DMS fluxes from the Gulf of Mexico. However, the generally low surface concentrations measured throughout the Gulf (mean of all surface samples = 2.5 nM), suggest that the area-normalized fluxes will be small in relation to other areas of the ocean such as polar and temperate seas where large-scale blooms of DMSP-producing phytoplankton occur (Barnard et al. 1983; Malin et al. 1993). Oligotrophic regions of the ocean typically have relatively low DMS and DMSP concentrations and display only modest seasonal variation (Kettle et al. 1999). Nonetheless, the oligotrophic regions make up a large fraction of the world ocean and therefore contribute significantly to global DMS flux to the atmosphere (Bates et al. 1992; Kettle et al. 1999). Although DMS concentrations in low nutrient water masses do not usually reach the spectacular levels sometimes found in temperate and polar seas, DMS concentrations in oligotrophic waters can reach concentrations of 5–12 nM, even though phytoplankton biomass and DMSP levels there are low (Dacey et al. 1998). It is interesting that we observed higher concentrations and a larger range of DMS concentrations in the oceanic sites as compared with the shelf sites (Fig. 6; Table 1). The reasons for DMS accumulation in phytoplankton-poor, oligotrophic waters are not well understood. Dacey et al. (1998) cited one possible reason for the late summer increase of DMS in the Sargasso Sea to be an increase in stratification and residence time of water in the

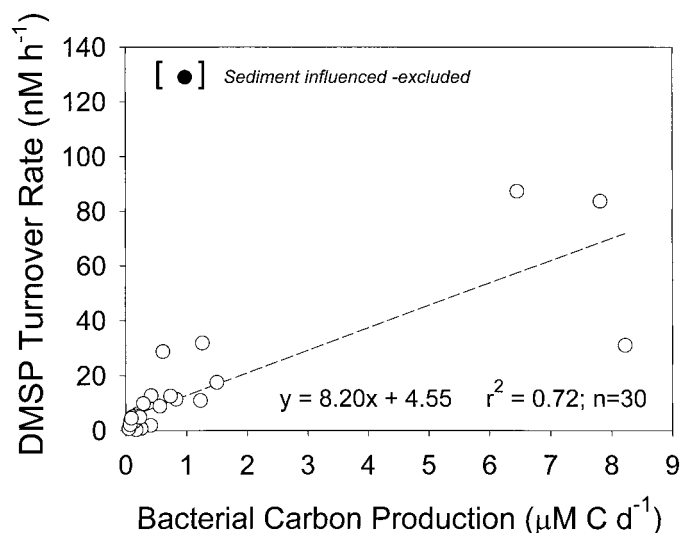


Fig. 7. Relationship between DMSPd turnover rate and bacterial carbon production (based on ^3H -thymidine incorporation rates) for all water samples collected in the northern Gulf of Mexico. The line represents the linear least-squares regression fit; $y = 8.205x + 4.55$; $r^2 = 0.72$; $n = 30$; $P \ll 0.001$. The point in brackets was excluded from the regression analysis based on its exceptionally high DMSPd concentration that may have been influenced by sampling very near the sediment.

upper high light environment. This situation would lead to bleaching of the colored DOM and a concomitant decrease in the photosensitized photodegradation of DMS. Intense photoinhibition of bacteria that consume DMS or an increase in the proportion of DMSP degraded to DMS (Ledyard and Dacey 1996) could also contribute to the seasonally elevated DMS concentrations in subtropical waters. Sampling at other times of the year and with much greater spatial coverage, would be required to determine if the Gulf of Mexico is a more significant source of sulfur to the regional atmosphere than is suggested by our small sample set.

DMSPd turnover rates and DMS concentrations—Previous studies of DMSPd turnover in both subtropical and temperate regions have utilized relatively long incubations (many hours) and added exogenous DMSP to concentrations well above natural levels (Kiene 1996b; Ledyard and Dacey 1996), or they have been carried out with water samples with extremely high (>1,000 nM) endogenous DMSP concentrations (Kwint and Kramer 1996). In our study, we used non-perturbing additions of ^{35}S -DMSP to trace the turnover of the natural pool of DMSPd. The rates of DMSP turnover measured with ^{35}S -DMSP (1–129 nM d⁻¹) fall in the same range (2–120 nM d⁻¹) as those reported in earlier studies that used loss kinetics of endogenous or added DMSPd in nearshore waters from the northern Gulf of Mexico (Kiene 1996b) or Vineyard Sound and the Sargasso Sea (Ledyard and Dacey 1996). In the present study, consistently low rates of DMSP turnover were measured in the oligotrophic oceanic waters (mean of 3.7 nM d⁻¹), whereas much higher rates (mean of 39 nM d⁻¹) were found in shelf waters (Table 1). Despite the tenfold range in mean DMSPd turnover between

Table 3. Average values* at each sampling station for the turnover times (τ) of DMSP pools and the calculated production rates and turnover times of DMS in the northern Gulf of Mexico.

Sites	Station No.	Mean DMSPd turnover rate [†] (nM d ⁻¹)	Mean τ DMSPd (d)	Mean τ DMSPp (d)	Calculated mean DMS production [‡] (nM d ⁻¹)	Mean τ DMS (d)
Shelf sites						
	8	12.6	0.26	1.2	1.3	2.0
	18	45.3	0.10	0.6	4.5	0.77
	23	58.5	0.03	0.4	5.9	0.43
Oceanic sites						
	2	2.7	0.59	3.3	0.27	10.5
	5	4.9	0.39	1.5	0.49	9.2
	10	1.7	0.46	10.3	0.17	9.1
	12	3.3	0.38	1.6	0.33	2.5
	14	7.5	0.26	1.3	0.75	2.4

* Values reported for each station are the means of 4 depth samples at each station, except for Sta. 14, at which only 3 depths were sampled.

[†] Turnover rates of DMSP were directly measured using tracer ³⁵S-DMSP.

[‡] DMS production was estimated by assuming that 10% of the DMSP turnover resulted in DMS production.

the oceanic and shelf sites, the mean DMS concentrations were virtually the same (2.0 vs. 2.1 nM respectively). There appeared to be a weak relationship between DMSP turnover and DMS concentration in the oceanic sites ($r^2 = 0.167$; $P = 0.08$) (Fig. 6), but this interpretation must be viewed with caution because there are relatively few data ($n = 19$) and only about 17% of the variation in DMS is explained by the regression. Somewhat surprisingly, there was no relationship at all between DMSP turnover and DMS concentration in the shelf sites; DMS fell within a very narrow range (0.8–2.9 nM) in the shelf waters despite high rates of DMSP turnover, which varied over 10-fold (Fig. 6). This lack of relationship is striking because DMSPd is generally considered to be the main precursor of DMS in the ocean (Turner et al. 1988; Kiene 1993). That DMS concentrations did not depend directly upon the rate of DMSP cycling in shelf waters, but showed some dependence in oligotrophic oceanic waters, is an intriguing observation and one that needs further verification. Many factors, including the low and variable yield of DMS during DMSPd degradation under in situ conditions (van Duyl et al. 1998) and the fact that DMS itself can turnover rapidly (Wolfe and Kiene 1993) probably contributed to the observed patterns.

DMSPd as a precursor of DMS—Previous studies suggested that DMS is only a minor product of DMSPd metabolism by bacterioplankton under most circumstances, especially in warm sub-subtropical waters (Kiene 1996a; Kiene and Linn in prep.). This raises the issue of whether conversion of DMSPd is indeed a major source of DMS in the oceans. We estimated the amount of DMS produced at each sampling station by using the measured DMSPd turnover rates and assuming that 10% of the DMSPd turnover resulted in DMS formation. We used 10% for the conversion efficiency of DMSPd into DMS because this was the mean value (range 2–21%) reported in a recent study of coastal and shelf waters from a variety of locations (Kiene and Linn in prep.). The calculated amounts of DMS that were produced from the DMSPd turnover at each station (mean values over depth) ranged from 0.2 to 5.9 nM d⁻¹ (Table 3). These DMS

supply rates yielded turnover times (τ) for the DMS pool that averaged 1.1 d for shelf stations and 7.0 d for oceanic stations (Table 3). These calculated turnover times are similar to those that have been estimated for biological turnover of DMS in coastal waters (Wolfe and Kiene 1993) and for oceanic waters in the equatorial Pacific (Kiene and Bates 1990; Kieber et al. 1996), or Sargasso Sea (Ledyard and Dacey 1996). These first-order calculations suggest that DMSPd turnover is sufficiently rapid to sustain DMS concentrations in the sea, even when only 10% of the DMSP turnover results in DMS production. This conclusion must be viewed with some caution because temporal and spatial differences in the conversion efficiency of DMSP into DMS (see Ledyard and Dacey 1996; van Duyl et al. 1998), and other factors such as the bacterial community structure (González et al. 1999), and rates of biological consumption, air-sea exchange and photochemical destruction of DMS (Kieber et al. 1996), would also affect the net DMS accumulations and steady state concentrations in the sea. Additionally, direct release from phytoplankton (Vairavamurthy et al. 1985), phytoplankton lyase activity (Stefels et al. 1995) and release during grazing or viral lysis (Dacey and Wakeham 1986; Wolfe and Steinke 1996; Malin et al. 1998) should be also be considered as potential mechanisms for DMS formation, in addition to bacterial conversion of DMSPd.

DMSP turnover and bacterial production—In a study of coastal Alabama waters, Kiene (1996b) concluded that DMSP degradation was primarily by bacterial size fractions (<1 μ m). On the other hand, Stefels et al. (1995) reported that the prymnesiophyte alga *Phaeocystis* sp., which produces a cell surface DMSP lyase, dominated DMSPd degradation to DMS in the early stages of a bloom in the North Sea. At the low nM DMSPd concentrations (0.2–10 nM) observed in the Gulf of Mexico, bacteria are likely to dominate DMSPd uptake and metabolism because natural marine bacterial populations have a high affinity uptake system for DMSP that operates with a half saturation constant in the low nM range (Kiene et al. 1998).

Because bacteria probably dominate DMSPd utilization, we looked for a relationship between DMSP turnover and bacterial production. A statistically significant relationship between DMSP turnover and bacterial production was observed (*see Fig. 7*), but the uneven data distribution (few points at intermediate values), and relatively low number of samples suggest that more data will be needed to firmly establish the relationship between bacterial growth rates and DMSP turnover rates. Several factors would probably improve our ability to discern such a relationship, if it exists. Complete accounting of DMSP transformation products produced during uptake assays would provide more accurate DMSP turnover rate constants. Our failure to measure dissolved nonvolatile transformation products during DMSP uptake rate assays led to an underestimation of the turnover rate and undoubtedly contributed to variability in the measurements. A better relationship between DMSPd turnover and bacterial growth might have been observed had we measured DMSP-S assimilation into bacterial macromolecules, rather than total turnover. This is because the sulfur of DMSP is incorporated into bacterial proteins and DMSP appears to be a major source of sulfur for bacterioplankton biomass production (Kiene et al. 1999; *see also below*). Factors affecting the growth of bacteria such as grazing and nutrient limitation might also have affected the relationship between DMSP turnover and bacterial production. For example, limitation of bacterial production by inorganic nutrients, especially phosphorus, has been reported for stations in the Gulf of Mexico very near those we sampled (*see Pomeroy et al. 1995*). However, it remains unclear how nutrient limitation will affect DMSP metabolism and this is certainly an area that needs investigation.

DMSPd as a carbon source for bacterioplankton—The contribution of DMSP-carbon to cellular carbon in some phytoplankton can be significant, ranging from 0 to 16% in different species (Matrai and Keller 1994). The contribution of DMSP to particulate carbon in the ocean is less well known, but evidence from the ratios of DMSPp to Chl *a* (nmol: μg) measured in oceanic waters suggest that DMSP makes up from 1–10% of the carbon in living phytoplankton (Kiene 1993; Bates et al. 1994), proportions similar to those observed in the culture studies (Matrai and Keller 1994). It is of interest then to learn whether DMSP could be a significant carbon source for bacteria in the sea. On the basis of the measured DMSP turnover rates and the bacterial carbon production (from the thymidine method) we estimated the contribution of DMSP turnover to the carbon demand of the bacterioplankton (Table 2). The contributions by DMSP to bacterial carbon demand ranged from 0.4 to 6.5% with mean values of 3.4 and 3.1% at the shelf and oceanic sites respectively (Table 2). Our calculations assume a BGE of 0.25 (moles of cell carbon produced/[moles of cell carbon produced + carbon respired]) and that all DMSP-carbon is utilized in the euphotic zone. The latter assumption is probably valid since little DMSP appears to be exported to depth (Bates et al. 1994), or to escape as volatile compounds to the atmosphere (Kiene 1993). Our thymidine-based carbon production estimates agree well with those reported for the

Gulf of Mexico near the Louisiana shelf (Biddanda et al. 1994).

Are the calculated contributions by DMSP to carbon cycling reasonable given the amounts of DMSP in the water column? We can make a rough estimation of how much phytoplankton carbon was in the form of DMSP by using DMSP:Chl *a* ratios found in Table 1, and by assuming phytoplankton contained 80 μg of C for every microgram of Chl *a* (Banse 1977). These calculations showed that DMSP comprised on average about 3.6% of the carbon in living phytoplankton biomass with values ranging from 0.3 to 7.8%. The mean value of 3.6% is very close to the estimated contributions of DMSP-carbon to daily bacterial carbon demand (3.1–3.4%) implying that phytoplankton DMSP turns over through the dissolved pool about once per day. By comparison, an average turnover time of ~ 2.5 d for the DMSPp pool is suggested by the turnover through the dissolved pool, although the range on these predictions is large (0.4–10.3 d) (Table 3). Although a $\sim 3.5\%$ contribution by DMSP to bacterial carbon demand is not overly large, it is significant because it is only a single compound, and very few compounds are known to contribute comparable amounts. Recognized major carbon sources for marine bacterioplankton include sugars, principally glucose (Rich et al. 1996), as well as total dissolved free and combined amino acids (Jorgensen et al. 1993). DMSP should be added to the list of labile, low molecular weight substrates that are important carbon sources to heterotrophic bacteria in the ocean.

Although there are uncertainties in the preceding calculations, the importance of DMSP to bacteria is likely to be even greater than what is suggested above because its contribution to carbon demand was probably underestimated in the present study because of limitations on the approach we used to quantify end-products in rate assays (*see above*). Also, DMSP appears to have additional functions in bacteria, which may include acting as a major source of reduced sulfur for protein synthesis (Kiene et al. 1999). Use of pre-reduced sulfur in the form of DMSP undoubtedly saves bacteria energy over use of oxidized sulfate but the overall significance of this in the energy budget of bacterioplankton remains to be determined. The importance of DMSP as a substrate for bacteria is further suggested by the fact that a wide variety of bacteria isolated from seawater are capable of degrading DMSP or by using it as a substrate for growth (Ledyard and Dacey 1994; Visscher and Taylor 1994; Yoch et al. 1997; González et al. 1999), and that DMSP-degrading bacteria often constitute $>10\%$ of the heterotrophic bacterial populations in the euphotic zone (Visscher et al. 1992).

Could DMSP be a quantitatively significant source of reduced sulfur for bacterioplankton?—A previous communication used data from surface water samples from the present study to argue that DMSP and its degradation product methanethiol, are potentially significant sources of reduced sulfur to marine bacterioplankton (Kiene et al. 1999). By using all the data, a plot of bacterial sulfur demand, versus measured DMSP turnover rate in the same samples, showed that for $\sim 90\%$ of the samples (28 out of 31) the amount of sulfur cycled through DMSP was greater than the sulfur demand by bacterioplankton (points above the 1:1 line in Fig. 8). In

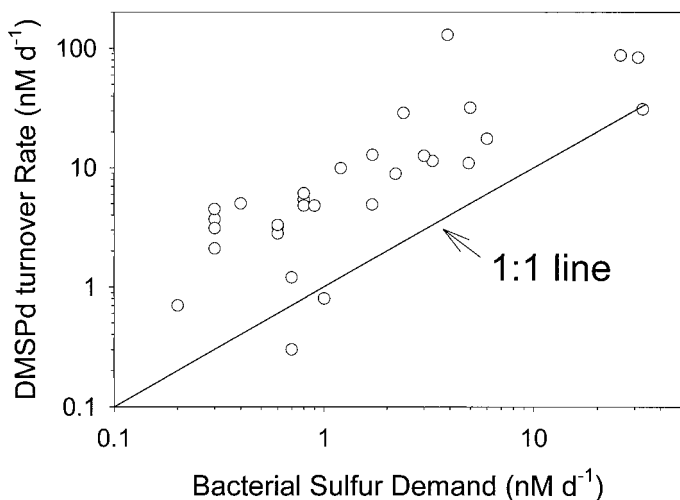


Fig. 8. Plot of DMSPd turnover rates vs. calculated bacterial sulfur demand for water samples throughout the northern Gulf of Mexico, September 1997. The bacterial sulfur demand was calculated from cell carbon production estimates and an assumed molar C:S ratio of 248 in bacteria. Each mole of DMSP contains 1 mol of sulfur. The line represents the 1:1 relationship. All but three of the points fall well above the line (note the log-log scale).

this case the sulfur demand was calculated from thymidine-derived cell carbon production and a bacterial C:S ratio of 248 (Cuhel et al. 1982). The potential contribution of DMSP to bacterial sulfur demand, averaged 670% and ranged from 42–3,300%; the highest value coming from the sediment-influenced sample at Sta. 18, which had a low bacterial production relative to DMSP turnover. In tests conducted after our 1997 cruise, it was found that approximately 15–40% of the sulfur from DMSP is assimilated into bacterial proteins during turnover in situ (Kiene et al. 1999; Kiene and Linn in prep.). If the conservative value of 15% is used for the DMSP assimilation efficiency, then the average contribution of DMSP to sulfur demand in the Gulf of Mexico samples was 97%, suggesting DMSP was an important, if not major source of reduced sulfur for bacterioplankton. Such a conclusion is contrary to the general notion that sulfate is the only significant source of sulfur for aquatic bacteria (Cuhel et al. 1982). As discussed in Kiene et al. (1999), marine bacteria apparently use the DMSP demethylation/demethiolation pathway to generate MeSH, which can be incorporated directly into methionine or oxidized to sulfate. The use of DMSP for a specific function (reduced sulfur source), in addition to its general use as a carbon substrate clearly makes DMSP a very important compound for marine bacteria. This finding helps to explain the high affinity uptake system for DMSP, which is expressed by natural populations (Kiene et al. 1998) and the widespread ability to metabolize DMSP by many diverse bacterial isolates (Ledyard and Dacey 1994; Visscher and Taylor 1994; de Souza and Yoch 1995; Yoch et al. 1997; González et al. 1999).

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